Research article

KINETIC STUDY OF THE METHYL CHLORIDE CONVERSION OVER THE H-ZSM5 ZEOLITE

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Abstract

The conversion of methyl chloride was one of many possibilities to reach hydrocarbon products. The solid H-ZSM5 with his specific morphology and acidic property gave the catalytic transformation. In other published papers, more details about the influence of some operating parameters on the activity of conversion were presented. To complete the given research of the mechanism to obtain the first C-C bond, a kinetic study was followed. **Copyright © www.acascipub.com, all rights reserved.**

Key words: the solid H-ZSM5, catalytic conversion, acidic property, kinetic study, coke deposit.

Introduction

Methane like oil spring is an important power supply. In literature, that molecule was converted to methyl chloride. After that, this one was easily transformed to hydrocarbons over the H-ZSM5 zeolite[1,2] . The present kinetic study helps us to follow the activity of the reaction in function of time and to see the steps of the decreasing activity.

Catalytic Activity

The catalytic material is synthesized by the method described by a patent of Mobil[3]. It is identified by the diffraction pattern. The reaction is carried out at atmospheric pressure with a fixed bed continuous micro reactor (0.8x25 cm quartz tube) with 200 mg catalyst. The results are obtained with different values of Si/Al which traduce different values of acidic form H-ZSM5. The solid contained in the reactor tube was heated in a programmable electric furnace under oxygen till 773 k. The products of the methyl chloride conversion are analyzed by gas chromatography with a column. We have two rates of the flow of gas (l/h) (mixture of the reactive with the nitrogen). The total pressure is always one atmosphere.

Results and Discussion

The catalytic testing gave results concerning the activity versus time. It is interesting to see that the equation which we develop further takes in account both the reactive concentration and the activity of the zeolite[4,5] represented by sites of OH. But preliminary, we have to present the context in which the transformation occurs. Physical elements like polarisability[6,7] or physical constraint factors of molecular groups explain the reaction. In methyl chloride molecule, the dimension of the orbital P of chlorine is important and the electronic cloud around the halogen becomes more diffused and more polarized. The recovery in transition state is more efficient because the orbital P of Chlorine is in recovering with the hybrid orbital SP^3 of carbon.

But we note a diminution of the force of the C-Cl bond inside the cavity of the solid because of the new electronic environment. The dipolar moment of the bond controls the chemical behavior of chlorine. In the acidic site Si-OH, the oxygen which is rich of electrons will attack the carbon which is positively polarized. Not far this phenomenon, the aluminum atom which is deficient of electrons will constitute a new bond with chlorine. Finally, we have exactly the manner of the breaking of C-Cl bond in methyl chloride in the solid. We have a dorsal substitution. This one is being in order 2 where there is no physical constrict (fig.1).

Fig 1: first step of conversion
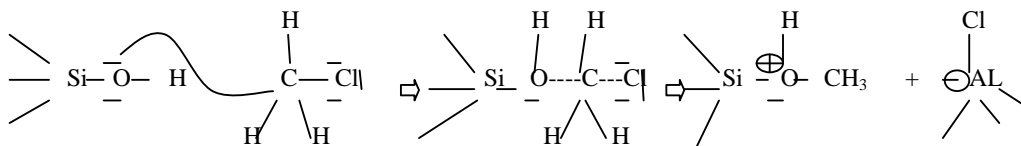
In the following expression of the rate, we have the term of reactive concentration and the term of acidic site.

$R = k (CH_3Cl) (HO)$

(CH_3Cl) is represented by P_{CH3CL} which appears further in tables 1, 2. But for (HO^-) of the site, we can to change it by (H^+).

$R = - d (CH_3Cl) / d t = k (CH_3Cl) (H^+)$

One reaction obeying this law is bimolecular. In the conversion of methyl chloride, the activity advances versus time. We think also that the acidic factor observes this tendency.

$d(H^+) = k_H d t => (H^+) = k_H t$

$R = - d(CH_3Cl) / d t = k (CH_3Cl) k_H t => - d(CH_3Cl) / ((CH_3Cl) = K t d t.$

$Log (CH_3Cl) = K t^2$ with $\{ K = - (k) (k_H) ; Integration between t = 0 and t.\}$

P_{CH3Cl} is the pressure of the effective converted reactive. The constant K depends of operating conditions. All this is verified by values given in catalytic testing and resumed[8] in tables 1, 2 giving respectively figures 2, 3 where we find effectively a linear and constant evolution of Log P_{CH3CL} versus t^2 followed by a decreasing. Through the values in tables 1,2 and figures2,3, two statements appear. The evolution is constant for two hours ($t^2 = 4 h^2$). Beyond this time, for the two cases, a falling of activity occurs because the solid undergoes a coke deposit coming from aromatic compounds[9] and their obstruction[10] of the channels and pores of the solid. The stability is evident for the two cases for the first two hours even we have strong operating conditions in the first case (table1 and fig.2).

Table 1: Conversion of CH_3Cl over 200mg of H-ZSM5 (Si / AL = 30)

T_R = 500 °C $\quad P^{CH3Cl}_{initial}$ = 760 mm Hg. $\quad$ Flow of gas: 0.5 l/h.

P^{CH3Cl}_{linear}	226.62	214.7	117.4	62.6
$P^{CH3Cl}_{aromatic}$	180.8	151.3	47.9	21.26
P^{CH3Cl}_{total}	407.4	366	165.3	83.9
Log P^{CH3Cl}_{total}	6.01	5.9	5.11	4.43
t (h)	1	2	4	5
t^2 (h^2)	1	4	16	25

Table 2: Conversion of CH_3Cl over 200mg of H-ZSM5 (Si / AL = 14)

T_R = 500 °C $\quad P^{CH3Cl}_{initial}$ = 76 mm Hg. $\quad$ Flow of gas: 5 l/h

P^{CH3Cl}_{linear}	24.8	21.8	20.5	11.4	8.6
$P^{CH3Cl}_{aromatic}$	9.7	7.9	5.3	3	2.1
P^{CH3Cl}_{total}	34.5	29.7	25.8	14.4	10.7
LogP^{CH3Cl}_{total}	3.54	3.39	3.25	2.67	2.37
t (h)	0.5	1	2	4	5
t^2 (h^2)	0.25	1	4	16	25

Fig2 : Log (P^{CH3Cl}_{total}) versus t^2

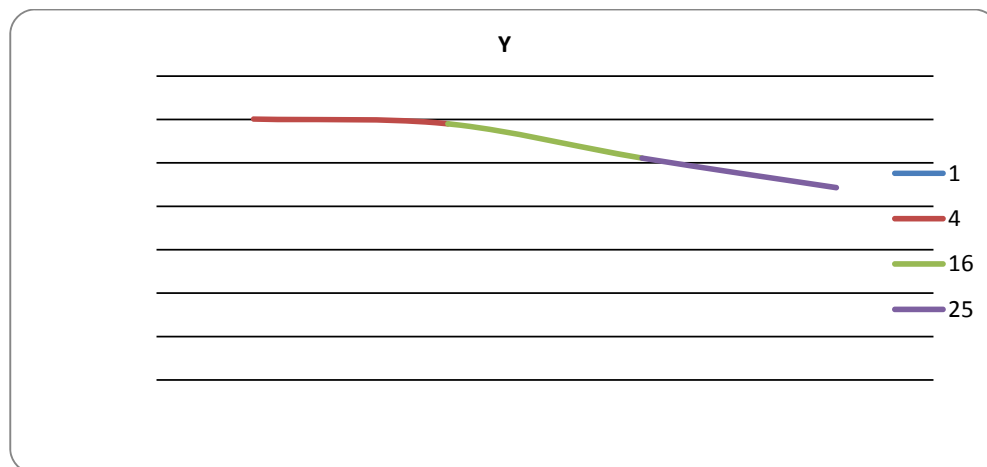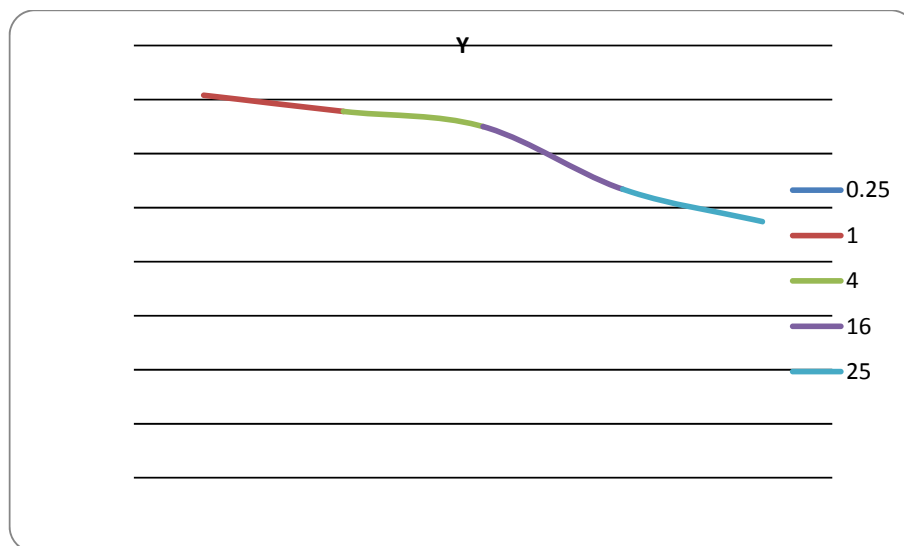**Fig3:** Log (P^{CH3Cl}_{total})   versus t^2

Conclusion

We note that for the first two hours, we have stability in the reaction. A regular decreasing occurs beyond this time. These results concern the two solid (table1, table2). To explain the phenomenon, we have to know that the acidic site permit a regular transformation of CH3Cl. But after two hours, the acidic sites of the solid are inhibited gradually. The explanation is the constitution of a hydrocarbon deposit occurring in cavities. In a precedent published work, I precise that we can use again the same solid present in the same reactor after burning all the deposit with a flow of oxygen all the night.

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